PATENT COOPERATION TREATY

From the
INTERNATIONAL PRELIMINARY EXAMINING AUTHORITY

To:
JENNIFER J. TAYLOR
WELL ST. JOHN P.S.
601 W. 1ST AVENUE,SUITE 1300
SPOKANE, WA 99201-3828

PCT

NOTIFICATION OF TRANSMITTAL OF INTERNATIONAL PRELIMINARY EXAMINATION REPORT

(PCT Rule 71.1)

Date of Mailing *(day/month/year)*	07 OCT 2004
Applicant's or agent's file reference 30-5082-PCT2	**IMPORTANT NOTIFICATION**

International application No.	International filing date *(day/month/year)*	Priority date *(day/month/year)*
PCT/US03/02106	24 January 2003 (24.01.2003)	24 January 2002 (24.01.2002)

Applicant

HONEYWELL INTERNATIONAL INC.

1. The applicant is hereby notified that this International Preliminary Examining Authority transmits herewith the international preliminary examination report and its annexes, if any, established on the international application.

2. A copy of the report and its annexes, if any, is being transmitted to the International Bureau for communication to all the elected Offices.

3. Where required by any of the elected Offices, the International Bureau will prepare an English translation of the report (but not of any annexes) and will transmit such translation to those Offices.

4. **REMINDER**

The applicant must enter the national phase before each elected Office by performing certain acts (filing translations and paying national fees) within 30 months from the priority date (or later in some Offices)(Article 39(1))(see also the reminder sent by the International Bureau with Form PCT/IB/301).

Where a translation of the international application must be furnished to an elected Office, that translation must contain a translation of any annexes to the international preliminary examination report. It is the applicant's responsibility to prepare and furnish such translation directly to each elected Office concerned.

For further details on the applicable time limits and requirements of the elected Offices, see Volume II of the PCT Applicant's Guide.

Name and mailing address of the IPEA/US Mail Stop PCT, Attn: IPEA/US Commissioner for Patents P.O. Box 1450 Alexandria, Virginia 22313-1450 Facsimile No. (703) 305-3230	Authorized officer Carl Whitehead Jr. Telephone No. 703-308-0956

Form PCT/IPEA/416 (July 1992)

PATENT COOPERATION TREATY

PCT

INTERNATIONAL PRELIMINARY EXAMINATION REPORT

(PCT Article 36 and Rule 70)

Applicant's or agent's file reference 30-5082-PCT2	**FOR FURTHER ACTION**	See Notification of Transmittal of International Preliminary Examination Report (Form PCT/IPEA/416)
International application No. PCT/US03/02106	International filing date *(day/month/year)* 24 January 2003 (24.01.2003)	Priority date *(day/month/year)* 24 January 2002 (24.01.2002)
International Patent Classification (IPC) or national classification and IPC IPC(7): H01L 23/48, 21/44 and US Cl.: 257/4, 751, 761, 764; 438/17, 592, 643, 653, 656, 685		
Applicant HONEYWELL INTERNATIONAL INC.		

1. This international preliminary examination report has been prepared by this International Preliminary Examining Authority and is transmitted to the applicant according to Article 36.

2. This REPORT consists of a total of 3 sheets, including this cover sheet.

   ☒ This report is also accompanied by ANNEXES, i.e., sheets of the description, claims and/or drawings which have been amended and are the basis for this report and/or sheets containing rectifications made before this Authority (see Rule 70.16 and Section 607 of the Administrative Instructions under the PCT).

   These annexes consist of a total of 8 sheets.

3. This report contains indications relating to the following items:

   - I ☒ Basis of the report
   - II ☐ Priority
   - III ☐ Non-establishment of report with regard to novelty, inventive step and industrial applicability
   - IV ☐ Lack of unity of invention
   - V ☒ Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement
   - VI ☐ Certain documents cited
   - VII ☐ Certain defects in the international application
   - VIII ☐ Certain observations on the international application

Date of submission of the demand	Date of completion of this report
21 August 2003 (21.08.2003)	03 August 2004 (03.08.2004)
Name and mailing address of the IPEA/US Mail Stop PCT, Attn: IPEA/US Commissioner for Patents P.O. Box 1450 Alexandria, Virginia 22313-1450 Facsimile No. (703) 305-3230	Authorized officer Carl Whitehead Jr. Telephone No. 703-308-0956

Form PCT/IPEA/409 (cover sheet)(July 1998)

INTERNATIONAL PRELIMINARY EXAMINATION REPORT

International application No.
PCT/US03/02106

I. Basis of the report

1. With regard to the **elements** of the international application:*

☐ the international application as originally filed.

☒ the description:
pages 1-17 as originally filed
pages NONE, filed with the demand
pages NONE, filed with the letter of _____.

☒ the claims:
pages NONE, as originally filed
pages 18-25, as amended (together with any statement) under Article 19
pages NONE, filed with the demand
pages NONE, filed with the letter of _____.

☒ the drawings:
pages 1-7, as originally filed
pages NONE, filed with the demand
pages NONE, filed with the letter of _____.

☐ the sequence listing part of the description:
pages NONE, as originally filed
pages NONE, filed with the demand
pages NONE, filed with the letter of _____.

2. With regard to the **language**, all the elements marked above were available or furnished to this Authority in the language in which the international application was filed, unless otherwise indicated under this item.
These elements were available or furnished to this Authority in the following language _____ which is:

☐ the language of a translation furnished for the purposes of international search (under Rule23.1(b)).

☐ the language of publication of the international application (under Rule 48.3(b)).

☐ the language of the translation furnished for the purposes of international preliminary examination(under Rules 55.2 and/or 55.3).

3. With regard to any **nucleotide and/or amino acid sequence** disclosed in the international application, the international preliminary examination was carried out on the basis of the sequence listing:

☐ contained in the international application in printed form.

☐ filed together with the international application in computer readable form.

☐ furnished subsequently to this Authority in written form.

☐ furnished subsequently to this Authority in computer readable form.

☐ The statement that the subsequently furnished written sequence listing does not go beyond the disclosure in the international application as filed has been furnished.

☐ The statement that the information recorded in computer readable form is identical to the written sequence listing has been furnished.

4. ☒ The amendments have resulted in the cancellation of:

☐ the description, pages NONE

☒ the claims, Nos. 77-78

☐ the drawings, sheets/~~fig~~ NONE

5. ☐ This report has been established as if (some of) the amendments had not been made, since they have been considered to go beyond the disclosure as filed, as indicated in the Supplemental Box (Rule 70.2(c)).**

** Replacement sheets which have been furnished to the receiving Office in response to an invitation under Article 14 are referred to in this report as "originally filed" and are not annexed to this report since they do not contain amendments (Rules 70.16 and 70.17).*

*** Any replacement sheet containing such amendments must be referred to under item 1 and annexed to this report.*

INTERNATIONAL PRELIMINARY EXAMINATION REPORT

International application No.
PCT/US03/02106

V. Reasoned statement under Rule 66.2(a)(ii) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement

1. STATEMENT

Novelty (N)	Claims	2-7, 9-34, 39, 42-76	YES
	Claims	1, 8, 35-38, 40, 41	NO
Inventive Step (IS)	Claims	16-34, 43-59, 65-76	YES
	Claims	1-15, 35-42, 60-64	NO
Industrial Applicability (IA)	Claims	1-76	YES
	Claims	NONE	NO

2. CITATIONS AND EXPLANATIONS

Claims 1, 8, 35-38, and 40-41 lack an inventive step under PCT Article 33(3) as being obvious over Hu (US 6,204,171). Hu (col. 6, line 42 - col. 10, line 57) discloses a nitride of a diffusion barrier, having at least a portion having a non-columnar grain structure. The nitrogen content can be adjusted.

Claims 2-7, 10-15, 39, 42, 60-62, and 64 lack an inventive step under PCT Article 33(3) as being obvious over Hu (US 6,204,171) in view of Hogan (US 6,156,647). Hu is applied as above and does not disclose the thickness of the thin film, nor the portions having non-columnar and columnar grain structures, nor using plasma. Hogan (col. 9, line 20 - col. 10, line 27) teaches a barrier layer at the claimed thickness which have portions that are non-columnar and columnar grain structures made in the presence of plasma, ablating material from the target. It would have been obvious to one of ordinary skill in the art at the time the invention was made to use the improvements of Hogan in Hu's process to prevent migration.

Claims 9 and 63 lack an inventive step under PCT Article 33(3) as being obvious over the prior art as applied in the immediately preceding paragraph and further in view of Wolf (Silicon Processing for the VLSI ERA). Hu and Hogan do not disclose the resistivity of the thin film. Wolf (pages 189-190, Table 4.3 on page 193) teaches that the resistivity of the thin films clearly is within the claimed range, and may be adjusted depending on the resistivity required.

Claims 16-34, 43-59, and 65-76 meet the criteria set out in PCT Article 33(2)-(3), because the prior art does not teach or fairly suggest the first and second layers of (TiQ)N, nor a copper barrier with a non-columnar and columnar grain structure having a substantial absence of amorphous phase material, nor the depositing of copper as claimed.

Claims 1-76 meet the criteria set out in PCT Article 33(4), and thus is useful for industrial applicability because the subject matter claimed can be made or used in industry.

CLAIMS

The invention claimed is:

1. A thin film comprising Zr, and N, at least a portion of the thin film having a non-columnar grain structure.

2. The thin film of claim 1 having a thickness of less than or equal to about 10 nm.

3. The thin film of claim 1 having a thickness, wherein a first portion of the thickness comprises the non-columnar grain structure and wherein a second portion of the thickness comprises columnar grains.

4. The thin film of claim 3 wherein the columnar grains have diameters of from about 10 nm to about 20 nm.

5. The thin film of claim 3 wherein the thin film is disposed over a silicon dioxide surface and wherein the first portion of the thickness is disposed closer to the silicon dioxide surface than is the second portion.

6. The thin film of claim 3, further comprising Ti.

7. The thin film of claim 6 having an atomic ratio of Ti to Zr greater than or equal to 1.0.

8. The thin film of claim 7 consisting essentially of Ti, Zr and N.

9. The thin film of claim 1 wherein the N is present in the thin film at from about 40 atomic percent to about 60 atomic percent.

10. The thin film of claim 1 having a resistivity of from about 69 μΩ•cm to about 106 μΩ•cm.

11. A barrier layer comprising Ti, Zr, at least a portion of the barrier layer comprising a non-columnar grain structure.

12. The barrier layer of claim 11 further comprising one or more elements selected from the group consisting of Al, Ba, Be, Ca, Ce, Cs, Hf, La, Mg, Nd, Sc, Sr, Y, Mn, V, Si, Fe, Co, Ni, B, C, La, Pr, P, S, Sm, Gd, Dy, Ho, Er, Yb, W, Cr, Mo, Nb, and Ta.

13. The barrier layer of claim 11 disposed between a metallic material and a

non-metallic material.

14. The barrier layer of claim 13 wherein the non-metallic material comprises a member of the group consisting of SiO_2 and low-k dielectric materials.

15. The barrier layer of claim 13 wherein the metallic layer comprises copper.

16. The barrier layer of claim 13 having a thickness of from about 10 nm to about 20 nm, wherein a first portion of the thickness comprises the non-columnar grain structure and wherein a second portion of the thickness comprises a columnar grain structure, the first portion of the layer being closer to the non-metallic material than is the second portion.

17. A metal diffusion barrier comprising:

a first layer comprising Ti and Q and being substantially nitrogen free, where Q comprises one or more elements selected from the group consisting of Al, Ba, Be, Ca, Ce, Cs, Hf, La, Mg, Nd, Sc, Sr, Y, Mn, V, Si, Fe, Co, Ni, B, C, La, Pr, P, S, Sm, Gd, Dy, Ho, Er, Yb, W, Zr, Cr, Mo, Nb, and Ta; and

a second layer comprising $(TiQ)_xN_z$.

18. The metal diffusion barrier of claim 17 wherein Q comprises Zr.

19. The metal diffusion barrier of claim 17 wherein the second layer is over the first layer, and further comprising a third layer over the second layer, the third layer comprising Ti and Zr and being essentially free of nitrogen.

20. The metal diffusion barrier of claim 17 wherein the first layer is over the second layer, and further comprising a third layer over the first layer, the third layer comprising $(TiQ)_xN_z$.

21. The metal diffusion barrier of claim 17 disposed between a metallic material and a non-metallic material.

22. A copper diffusion barrier comprising a bi-layer, a first portion of the bi-layer comprising TiZr, and a second portion of the bi-layer comprising $(TiZr)_xN_z$.

23. The copper diffusion barrier of claim 22 wherein the second portion comprises non-columnar grain structure.

24. The copper diffusion barrier of claim 22 wherein the second portion is adjacent a layer of silicon dioxide and the first portion is adjacent a copper based

material.

25. A titanium-comprising material having an electrical resistivity of from about 69 μΩ•cm to about 106 μΩ•cm, and having a substantially uniform thickness.

26. The titanium-comprising material of claim 25 further comprising Zr.

27. The titanium-comprising material of claim 26 having an atomic ratio of Ti to Zr of greater than or equal to 1, and further comprising from about 40 atomic percent to about 60 atomic percent N.

28. The titanium-comprising material of claim 25 further comprising N.

29. A copper barrier film having a first portion comprising a non-columnar grain structure, and a second portion comprising a columnar grain structure, the film having a substantial absence of amorphous phase material.

30. The film of claim 29 comprising Ti.

31. The film of claim 29 comprising Zr.

32. The film of claim 29 comprising Ti, Zr and N.

33. The film of claim 29 consisting essentially of $(TiZr)_xN_z$, where x = 0.40-0.60 and z = 0.40-0.60.

34. The film of claim 18 having an electrical resistivity of from about 69 μΩ•cm to about 106 μΩ•cm.

35. The film of claim 29 having a thickness of less than 20 nm.

36. A diffusion protected surface comprising:

a material having a surface; and

a thin film comprising Zr and N over the surface, at least a portion of the thin film having a non-columnar grain structure.

37. The diffusion protected surface of claim 36 wherein the thin film further comprises Ti.

38. The diffusion protected surface of claim 36 wherein the material having the surface comprises a non-metallic material.

39. The diffusion protected surface of claim 36 wherein the material having the surface comprises SiO_2.

40. The diffusion protected surface of claim 36 wherein the thin film is disposed between the surface and a metallic material comprising one or more of Cu, Ag, Sn, Mg and Al.

41. A structure comprising:

a silicon substrate;

a insulative material over the substrate;

a barrier layer comprising $(TiZr)_xN_z$ over the insulative material, the barrier layer having a substantial absence of amorphous structure, at least a portion of the barrier layer comprising non-columnar grain structure; and

a layer comprising a metal over the barrier layer.

42. The structure of claim 41 wherein the barrier layer consists essentially of $(TiZr)_xN_z$.

43. The structure of claim 41 wherein x = 0.44-0.60 and z = 0.40-0.60.

44. The structure of claim 41 wherein the metal comprises copper.

45. The structure of claim 41 wherein the metal comprises copper, wherein the insulative material comprises SiO_2; wherein the barrier layer has a thickness of less than or equal to about 5 nm; and wherein, the barrier layer substantially prevents diffusion of copper from the layer comprising the metal into the SiO_2 during heat treatment of the structure at a temperature of about 650°C for about 1 hour.

46. The structure of claim 41 wherein the metal comprises copper, wherein the insulative material comprises SiO_2; wherein the barrier layer has a thickness of less than or equal to about 20 nm; and wherein, the barrier layer substantially prevents diffusion of copper from the layer comprising the metal into the SiO_2 during heat treatment of the structure at a temperature of about 700°C for about 5 hours.

47. A microelectronic device comprising:

a insulative material comprising an opening having a bottom surface and a sidewall surface;

a barrier layer over the bottom surface, the barrier layer comprising Ti and Zr, and having an electrical resistivity of less than or equal to about 69 μΩ•cm to about 106 μΩ•cm; and

a material comprising copper disposed over the barrier layer.

48. The microelectronic device of claim 47 wherein the opening has a width of less than or equal to about 350 nm.

49. The microelectronic device of claim 47 wherein the opening has a width of less than or equal to about 100 nm.

50. The microelectronic device of claim 47 wherein the barrier layer is disposed over the sidewall surface.

51. The microelectronic device of claim 50 wherein the barrier layer has a substantially uniform thickness over the bottom surface and over the sidewall surface.

52. The microelectronic device of claim 51 wherein the opening has a height to width aspect ratio of greater than or equal to 1.

53. The microelectronic device of claim 52 wherein the aspect ratio is greater than 2.

54. The microelectronic devise of claim 51 wherein thickness is less than or equal to about 20 nm..

55. The microelectronic devise of claim 51 wherein thickness is less than or equal to about 5 nm.

56. The microelectronic devise of claim 47 wherein the barrier layer comprises an atomic ratio of Ti to Zr of greater than or equal to 1.0.

57. The microelectronic devise of claim 47 wherein the barrier layer further comprises N.

58. The microelectronic device of claim 57 wherein the barrier layer comprises from about 40 atomic percent to about 60 atomic percent N.

59. The microelectronic device of claim 57 wherein the barrier layer consists essentially of Ti, Zr and N.

60. The microelectronic device of claim 57 wherein the barrier layer consists of Ti, Zr, and N.

61. The microelectronic device of claim 47 wherein the material comprising

copper consists essentially of copper.

62. A method of forming a barrier layer comprising:

providing a substrate comprising a material to be protected;

providing a target comprising Ti; and

in the presence of an Ar/N_2 plasma, ablating material from the target onto the substrate at a deposition power of from about 2 kW to about 9 kW, the ablating forming a barrier layer comprising Ti and N and having a substantially uniform thickness over at least a portion of the material to be protected.

63. The method of claim 62 wherein the target further comprises at Zr.

64. The method of claim 62 wherein the barrier layer further comprises Zr, the barrier layer having an atomic ratio of Ti to Zr of greater than or equal to about 1.

65. The method of claim 62 wherein the barrier layer has an electrical resistivity of from about 69 μΩ•cm to about 106 μΩ•cm.

66. The method of claim 62 further comprising depositing a conductive material over the barrier layer, the conductive material comprising a metal.

67. A method of forming a microelectronic device, comprising:

providing a substrate having one or more gap structures formed in an insulative material;

lining the gap structures with a layer comprising Ti, the layer having a substantially uniform thickness and having an electrical resistivity of from about 69 μΩ•cm to about 106 μΩ•cm;

depositing a copper material over the layer.

68. The method of claim 67 wherein the layer further comprises N and one or more elements selected from the group consisting of Al, Ba, Be, Ca, Ce, Cs, Hf, La, Mg, Nd, Sc, Sr, Y, Mn, V, Si, Fe, Co, Ni, B, C, La, Pr, P, S, Sm, Gd, Dy, Zr, Ho, Er, Yb, W, Cr, Mo, Nb, and Ta.

69. The method of claim 68 wherein the layer consists essentially of Ti, Zr and N.

70. The method of claim 67 wherein the one or more gap structures comprise openings having a height to width aspect ratio of greater than or equal to 4.

71. The method of claim 70 wherein the openings have a width of less than or equal to about 350 nm.

72. The method of claim 70 wherein the openings have a width of less than or equal to about 200 nm.

73. The method of claim 70 wherein the openings have a width of less than or equal to about 100 nm.

74. The method of claim 67 wherein the insulative material comprises SiO_2.

75. A method of forming a protected surface comprising:

providing a substrate having a surface into a reaction chamber;

providing a target within the reaction chamber, the target consisting essentially of Ti and Zr;

ablating material from the target onto the surface in the presence of nitrogen to deposit a first layer over the surface; and

ablating material from the target in an absence of added nitrogen to form a second layer over the first layer.

76. The method of claim 75 wherein the surface comprises silicon dioxide.

77. The method of claim 75 wherein the first layer has a thickness of less than or equal to about 10 nm, and has a microstructure consisting essentially of non-columnar grains.

78. The method of claim 75 wherein the first layer has a thickness of greater than about 10 nm, and comprises a first portion having non-columnar grain structure and a second portion comprising columnar grain structure.